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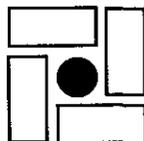
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## Electronic Spectra of Heptafluoro-2-naphthol and Its Complexes with Amines in a Low-Temperature Matrix and in Supersonic Jet

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In experimental studies of intermolecular potential energy surfaces of hydrogen-bonded complexes, those data are especially valuable that are obtained in the gas phase, i.e., in the absence of distorting interactions with the molecular environment, and at low temperatures, at which the conformational heterogeneity of complexes is least pronounced and the excited rovibrational energy levels are least populated [1, 2]. For complexes with strong hydrogen bonding, in which intermolecular proton transfer is possible, the above requirements are particularly incompatible, because ionic compounds are usually characterized by very low vapor pressures. In this work, we attempted structure elucidation of heptafluoronaphthol ( $C_{10}F_7OH$ ) complexes with ammonia and triethylamine by the electronic absorption and emission spectroscopy in supersonic jet and in argon matrix.

Heptafluoronaphthol is an effective proton donor for hydrogen bonds [3] and forms ionic pairs by proton transfer in its molecular complexes with aliphatic amines in hydrocarbon solvents [4]. However, proton transfer was not detected in such complexes in the gas phase at 440 K under static conditions [5]. Supersonic jets are characterized by a translational temperature of ~15–20 K, rotational temperature of 2–3 K, and vibrational temperature in between these values. Thus, the vibronic structure of electron transitions is observable at line widths of 1–2  $cm^{-1}$ , and its analysis can provide reliable information on the structure of

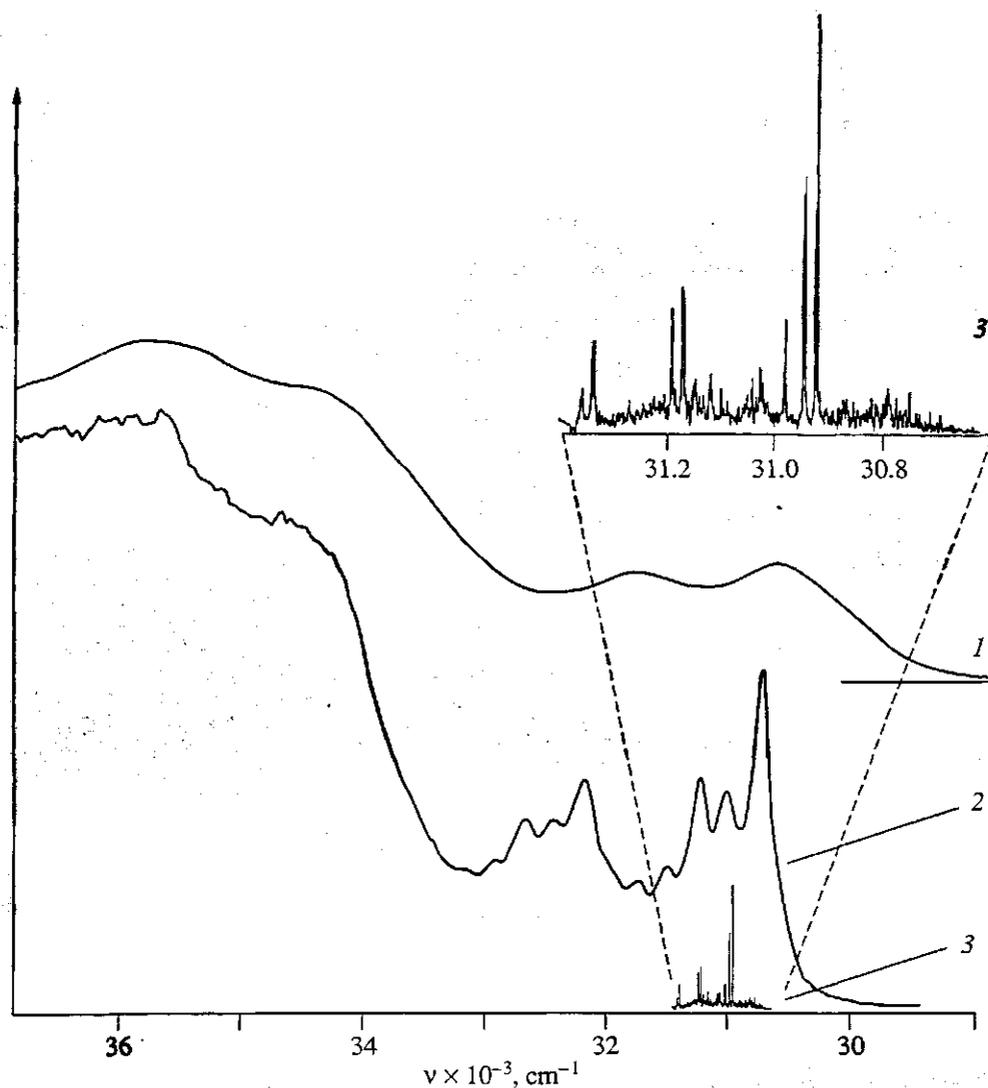
the complexes. Energy level perturbations of matrix-isolated complexes are small, which results in spectral patterns that resemble those in the gas phase and hydrocarbon solvents. As the vibrational spectra of perfluoronaphthols were not studied previously, we had to begin with the interpretation of the vibrational structure and search for the criteria of hydrogen bond formation and ionization of the complexes. A comparison with naphthols  $C_{10}H_7OH$  was deemed quite useful, because the excited-state intermolecular proton transfer in complexes of these compounds is thoroughly studied by spectral methods in both low-temperature matrices and supersonic jet [6–9].

The key experiments were carried out with heptafluoro-2-naphthol (2-FN)  $2-C_{10}F_7OH$  synthesized as described in [10]. According to [4, 5], the absorption bands of the neutral and ionized forms of this compound are more suitably arranged for the detection of proton transfer than in 1-FN. Moreover, the energy and spectral parameters of the two possible rotamers less differ in 2-FN than in 1-FN, which facilitates the interpretation of the spectra [3]. Transmission and fluorescence spectra were recorded in an argon matrix at 9–10 K. Samples were prepared by passing a flow of either pure argon or argon mixed with 2.5–8% of an acceptor through a cell containing FN at ~50°C and freezing it on a sapphire window at 20 K. Fluorescence excitation spectra were obtained using the second harmonic of a dye laser with the excitation by an excimer XeCl laser ( $\Lambda$ -Physik). The spectral resolution in the absorption and emission spectra was ~2 and 20  $cm^{-1}$ , respectively. The technique of spectral measurements has been described in detail in [11]. The gas-phase fluorescence excitation and emission spectra were obtained using a supersonic jet of FN-containing helium outflowing through a nozzle 0.2 mm in diameter at the pressure drop of 2 atm. The excitation was performed 5 mm downstream from the nozzle by a dye laser with frequency doubling excited by a pulse Nd:YAG laser. The integrated luminescence in the excitation

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**Fig. 1.** (1, 2) Absorption and (3, 3') fluorescence excitation spectra of heptafluoro-2-naphthol in (1) a heptane solution at 300 K, (2) argon matrix at 12 K, and (3) supersonic jet with the integrated fluorescence recorded in the range  $\nu < 30\,000\text{ cm}^{-1}$ ; (3') is an expansion of 3.

spectra was recorded using filters that transmitted in the spectral ranges above 335 and 400 nm. The fluorescence spectra were recorded at the resolution  $20\text{--}100\text{ cm}^{-1}$ .

The vibrational structure of the absorption spectrum of 2-FN in argon matrix is much better resolved than that of hydrocarbon solvents at room temperature (Fig. 1). The  $O_0$  transition is at  $30\,800\text{ cm}^{-1}$ . In the high-frequency region, the vibronic bands were observed at 270, 490, and  $1\,430\text{ cm}^{-1}$ , which correspond to the naphthalene ring vibrations. In the vibrational energy range above  $2\,500\text{ cm}^{-1}$ , the spectrum becomes diffuse, and the whole pattern undergoes a slight blue shift as compared to the spectrum obtained in a heptane solution. Figure 1 also shows the fluorescence excitation spectrum obtained in supersonic jet in

the range  $30\,500\text{--}31\,400\text{ cm}^{-1}$ . It is seen that further narrowing of the spectral lines and their hypsochromic shift by  $\sim 100\text{ cm}^{-1}$  compared to the matrix-isolation spectrum occur under these conditions in the absence of perturbations. The most intense band, at  $30\,911\text{ cm}^{-1}$ , corresponds to the  $O_0$  transition in the *cis* rotamer of 2-FN, in which the hydroxyl group is oriented towards the fluorine in position 1. The bands on the high-frequency side correspond to the vibronic transitions involving low-frequency vibrations of the C-F groups and the naphthalene ring. In the spectrum of 2-naphthol  $\text{C}_{10}\text{H}_7\text{OH}$ , the  $O_0$  transition is at  $30\,905\text{ cm}^{-1}$  [12]; a slight shift of the electron transition frequency upon fluorination of the ring is, according to [13], the general feature of perfluorinated aromatic compounds. In the supersonic-jet fluorescence excitation spectrum, there

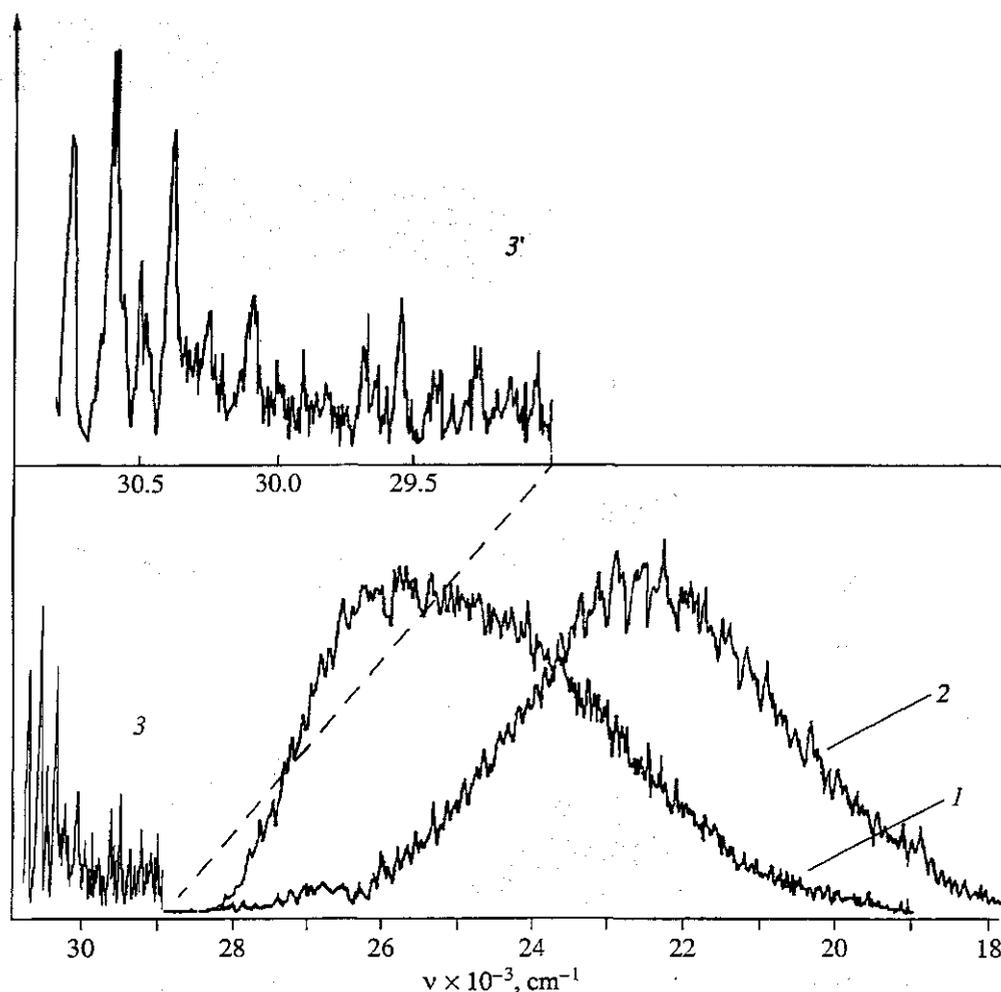


Fig. 2. The fluorescence spectra of heptafluoro-2-naphthol in (1) argon matrix ( $\nu_{\text{exc}} = 30800 \text{ cm}^{-1}$ ), (2) argon matrix in the presence of 2.5%  $\text{NH}_3$  ( $\nu_{\text{exc}} = 29850 \text{ cm}^{-1}$ ), and (3) supersonic jet ( $\nu_{\text{exc}} = 30911 \text{ cm}^{-1}$ ); (3') is an expansion of 3.

is also a set of weak bands on the low-frequency side of the  $O_o$  band. By analogy with [8], they were assigned to the *trans* rotamer, in which the hydroxyl group is oriented towards the fluorine in position 3, and the band at  $30518 \text{ cm}^{-1}$  was assigned to the  $O_o$  transition of this rotamer. A comprehensive analysis of the vibrational structure of these spectra will be reported elsewhere.

The fluorescence spectrum of matrix-isolated 2-FN is structureless (Fig. 2). Both the location and the shape of the emission band much resemble those of the emission bands observed in the spectra of 2-FN in a hydrocarbon solvent and in the gas phase [5]. The excitation and transmission spectra practically coincide in the  $30000\text{--}31800 \text{ cm}^{-1}$  range. Thus, unlike naphthol  $\text{C}_{10}\text{H}_7\text{OH}$ , 2-FN gives the fluorescence spectrum that qualitatively differs from the absorption spectrum.

The emission spectrum obtained in supersonic jet upon excitation of the  $30911 \text{ cm}^{-1}$  band of the *cis* rotamer has a line structure (Fig. 2) and resembles

the spectrum of perfluoronaphthalene [14]. At a distance of  $1500\text{--}2000 \text{ cm}^{-1}$ , the vibronic components become too much overlapped for the spectral lines to be unambiguously discriminated. Upon excitation of the most intense band of the *trans* rotamer at  $30716 \text{ cm}^{-1}$ , the emission spectrum exhibits a broad structureless band with a maximum of approximately  $26500 \text{ cm}^{-1}$ . This indicates that the properties of the excited state depend highly on the features of the intra-molecular interaction between the hydroxyl group and the adjacent substituent atom.

The excitation and fluorescence spectra of 1-FN in supersonic jet also exhibit two electronic origins caused by the presence of the two rotamers. The OH group of the more stable *cis* rotamer forms an intramolecular bond with the fluorine in position 8 [3], and the  $O_o$  transition in this structure is at  $30542 \text{ cm}^{-1}$ , whereas, in 1-naphthol, it is at  $31181 \text{ cm}^{-1}$  [8]. In the *trans* rotamer, the  $O_o$  transition is observed at  $30753 \text{ cm}^{-1}$ .

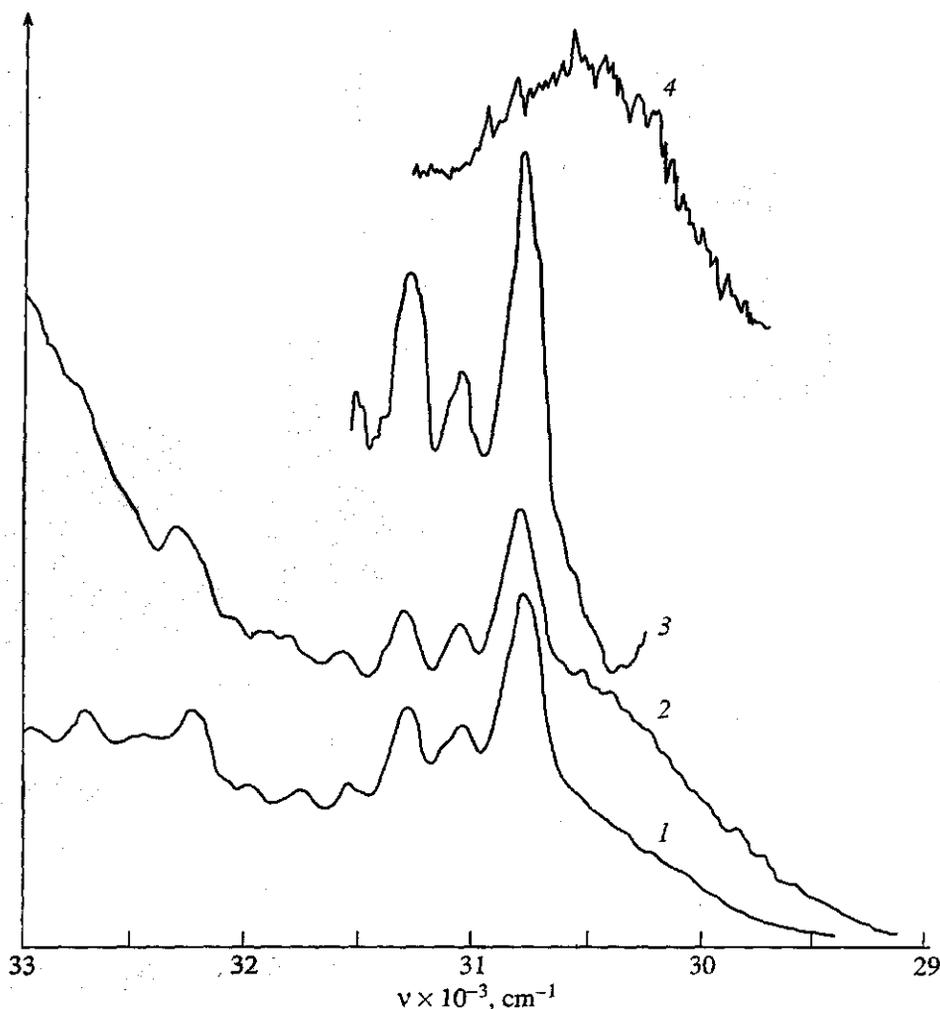


Fig. 3. (1, 2) Absorption and (3, 4) fluorescence excitation spectra of heptafluoro-2-naphthol in an argon matrix in the presence of  $\text{NH}_3$ : (1) 2.5%  $\text{NH}_3$ ; (2) 5%  $\text{NH}_3$ ; (3) 2.5%  $\text{NH}_3$ ,  $\nu_{\text{rec}} = 28000 \text{ cm}^{-1}$ ; and (4) 2.5%  $\text{NH}_3$ ,  $\nu_{\text{rec}} = 23000 \text{ cm}^{-1}$ .

In the spectrum of 2-FN coprecipitated with ammonia in an argon matrix, there is a broad structureless absorption band shifted to lower frequencies (Fig. 3). This absorption increases with the ammonia content, and the bands of free 2-FN against its background gradually decrease. The shape of this absorption band resembles the spectra of 2-FN anion in aqueous and hydrocarbon solutions [4], which suggests the ion-pair structure of the 2-FN-ammonia complex. The complexes with the  $\text{OH}\cdots\text{N}$  hydrogen bond do not form in considerable quantities, as the spectrum exhibits no bands with a bathochromic shift by 150–250  $\text{cm}^{-1}$  characteristic of such complexes [4]. The spectra of the system containing 2-FN and triethylamine, which is a stronger base than ammonia, have the same appearance.

The luminescence spectrum of the complex obtained by excitation at the long-wave edge of the absorption band, where the overlap with the band corresponding to neutral 2-FN is minimal, exhibits a broad structureless band centered at approximately

22500  $\text{cm}^{-1}$  (Fig. 2) similar to that observed in a dodecane solution [5]. Upon excitation at 30785  $\text{cm}^{-1}$ , which corresponds to the maximum of the band of free 2-FN, the emission spectrum shows two bands from free 2-FN and its anion. This is caused by a strong overlap of the free 2-FN band with the absorption of the anion. By recording the emission at the long-wave luminescence edge of the anion, the part of the excitation spectrum that characterizes the absorption of the anion can be observed without overlapping with the band from the neutral 2-FN (Fig. 3, curve 4). On the contrary, by measuring the emission at the short-wave edge of the luminescence band, it is possible to obtain an excitation spectrum identical to the absorption spectrum of matrix-isolated 2-FN (Fig. 3, curve 3).

Thus, the formation of 2-FN complexes with ammonia and triethylamine in an argon matrix is accompanied by intermolecular proton transfer through the  $\text{OH}\cdots\text{N}$  hydrogen bond, as it is in hydrocarbon solvents. To clarify the role of environment, it is highly desirable to investigate the gas-phase structure of the complex

at low temperatures, because the number of such complexes known to exist in the gas phase as ion pairs is rather small [15]. However, interaction with proton acceptors ( $H_2O$ ,  $NH_3$ ,  $Et_2O$ , and  $Et_3N$ ) sharply decreases the fluorescence yield of 2-FN; therefore, we failed to obtain the excitation spectra of such complexes in supersonic jet with an acceptable signal-to-noise ratio.

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